Notes

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Shin-ichi Sasaki,[*1] Shohei Aoyagi,[*1] and Hong-Yeng Hsü[*2] : The Isolation of Taraxerol, Taraxeryl Acetate, and Taraxerone from *Crossostephium chinense* MAKINO (Compositae).

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Koo and Tchan[1] have reported the isolation of a substance melting at 254~255.5° from the root of *Crossostephium chinense* MAKINO (Compositae), which is one of the most popular Chinese herbs in Formosa. This paper describes the isolation and identification of taraxerol, taraxeryl acetate, and taraxerone from the petroleum ether extract of this plant.

Extraction of the dried and powdered root and stem with petroleum ether, followed by chromatographic separation of the crude material on silica gel with chloroform gave three crystalline substances, A, B, and C, in a ratio of 8:1:6. Compound A, $C_{32}H_{52}O_2$, ν_{max}^{KBr} 1724 and 1253 cm^{-1}[*3] (acetate), was hydrolyzed to Compound C. Compound B, $C_{30}H_{48}O$, ν_{KBr}^{max} 1708 cm^{-1} (ketone), also gave Compound C upon reduction with lithium aluminum

TABLE I.

	m.p. (°C)[*4]	$[\alpha]_D$[*5]		Taraxerol and derivatives m.p. (°C)	$[\alpha]_D$	ref.
Compound A :	297~299	+ 8°	acetate :	298~299	+14°	2)
				297	+ 8	3)
				304~305	+ 9	4)
				303~307		5)
Compound B :	233~236	+12	ketone :	241~243	+12	2)
				240~241	+12	4)
				245~249	+12	5)
Compound C :	273~275		alcohol :	279~281	+ 3	2)
				270		3)
				282~283	+ 3	4)
				278~280	+ 2	5)
Benzoate of Compound C :	283~284	+33	benzoate :	287~289	+36	2)
				284	+36	3)
				292~293	+37	4)
				288~289	+34	5)

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[*3] Infrared spectra were measured with a Hitachi Infrared Spectrophotometer Model EPI-S.
[*4] All melting points are uncorrected.
[*5] Measured in chloroform.

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hydride. Compound C, $C_{30}H_{50}O$, is an alcohol and was converted to Compound B by chromic acid oxidation. Their melting points and specific rotations are very similar to those of taraxerol and the derivatives as shown in the Table I.

Final confirmation was made by the infrared spectra of Compound C and taraxerol*6 which were superimposable and, therefore, Compound A and B are taraxeryl acetate and taraxerone, respectively.

Experimental

Extraction and Chromatographic Separation——The dried and powdered root and stem (8.5 kg.) were refluxed in petr. ether (b.p. 40~100°) for 2 hr. three times to give 14.8 g. of a crude mixture. A portion (790 mg.) of the sample that was recrystallized once from petr. ether was chromatographed on 35 g. of silicic acid with chloroform, and several fractions were checked by IR spectrum and thin-layer chromatography. Compound A (400 mg.), B (50 mg.), and C (300 mg.) were eluted in turn and then recrystallized from a small amount of chloroform.

Compound A——Colorless needles. *Anal.* Calcd. for $C_{32}H_{52}O_2$: C, 81.99; H, 11.18; mol. wt., 468.7. Found: C, 82.02; H, 10.74; mol. wt., 473.

Compound B——Colorless plates. *Anal.* Calcd. for $C_{30}H_{48}O$: C, 84.84; H, 11.39. Found: C, 85.09; H, 11.39.

Compound C——Colorless needles. *Anal.* Calcd. for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found: C, 84.17; H, 11.83.

Hydrolysis of Compound A——Compound A (100 mg.) was hydrolyzed with refluxing 0.06*N* NaOH in ethanol (15 ml.) for 4 hr. to yield Compound C (68 mg.).

Reduction of Compound B——Reduction of Compound B (50 mg.) with excess $LiAlH_4$ in ether was carried out according to the usual procedure giving 37 mg. of Compound C.

Oxidation of Compound C——Compound C (190 mg.) was oxidized in the usual manner using CrO_3 (130 mg.)//pyridine (8 ml.) complex to give Compound B (160 mg.).

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Shun-ichi Yamada, Takayuki Shioiri, Taisuke Itaya, Takeshi Hara, and Rei Matsueda: Ind.-N-Alkylation of Tryptophan and Synthesis of 1-Alkyltryptophan Hydrazides.

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During the course of an investigation of the synthetic approaches to the indole alkaloids, it became desirable to obtain 1-alkyltryptophans,*2 some of which were synthesized by rather troublesome methods.[1~3]

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*2 DL-form, unless otherwise stated.

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